

This is a postprint version of the following published document:

González-Benito, J., Castillo, E. and Cruz-Caldito, J.F (2015). Determination of the linear coefficient of thermal expansion in polymer films at the nanoscale: influence of the composition of EVA copolymers and the molecular weight of PMMA. *Phys. Chem. Chem. Phys.*, 2015,17, 18495-18500

doi: <https://doi.org/10.1039/C5CP02384J>



Journal Name

ARTICLE

Determination of the linear coefficient of thermal expansion in polymer films at nanoscale. Influence of composition in EVA copolymers and molecular weight in PMMA

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

J. González-Benito*, E. Castillo and J.F. Cruz-Caldito

Nanothermal-expansion of poly(ethylene-co-vinylacetate), EVA, and poly(methyl methacrylate), PMMA, in the form of films was measured to finally obtain linear coefficients of thermal expansion, CTE. The simple deflection of a cantilever in an atomic force microscope, AFM, was used to monitor thermal expansions at nanoscale. The influences of: a) the structure of EVA in terms of its composition (vinylacetate content) and b) the size of PMMA chains in terms of the molecular weight were studied. To carry out this, several polymer samples were used, EVA copolymers with different weight percents of the vinylacetate comonomer (12, 18, 25 and 40%) and, PMMA polymers with different weight average molecular weights (33.9, 64.8, 75.600 and 360.0 kg/mol). The dependences of the vinyl acetate weight fraction of EVA and the molecular weight of PMMA on their corresponding CTEs were analyzed to finally explain them with new, intuitive and very simple models based on the rule of mixtures. In the case of EVA copolymers a simple equation considering the weighted contributions of each comonomer was enough to estimate the final CTE above the glass transition temperature. On the other hand, when the molecular weight dependence is considered the free volume concept was used as novelty. The expansion of PMMA, at least at nanoscale, was well and easily described by the sum of the weighted contributions of the occupied and free volumes respectively.

1. Introduction

When different materials are joined to prepare certain parts of final products, their thermal and mechanical properties play very important roles respect to the structural integrity for the in service behaviour. For example, a mismatch between certain properties of materials such as the coefficient of thermal expansion, CTE, could cause feasibility and reliability problems. Besides, CTE is also essential for mechanical and thermal stress modeling studies. Due to this, efforts should be focused on understanding the changes of CTE caused by structural, morphological and compositional variations in the material systems. With this knowledge, the material design could be more easily done.

It is well known that large positive thermal expansion in polymers is one of the major drawbacks when using them for applications where the sample dimensions play an important role. Therefore, understanding and controlling of the CTE in polymers is an important issue that should be overcome.

Most of the solid materials are expanded when heated and shrunk when cooled. For a solid material the change of size in one dimension, length change (ΔL), for a particular change of temperature can be expressed as follows:

$$\frac{\Delta L}{\Delta T} = \alpha_L \cdot L_0 \quad (1)$$

Where L_0 is the initial length at temperature T_0 , α_L is the linear coefficient of thermal expansion or CTE and ΔT is the change of temperature for which a linear expansion of ΔL occurs. When atomic or molecular scales are considered, the thermal expansion arises from the increase of the mean separation between atoms in the material. Qualitatively it could be said that the stronger the interatomic bond, the deeper and narrower its potential curve. This would mean therefore that for a certain increase of temperature the increase in the interatomic separation should be smaller and the value of CTE as well. However, this explanation is only applicable to very simple systems such as monoatomic substances at their thermodynamical equilibrium. It is evident that for more complex materials the behavior in terms of thermal expansion should take into consideration other contributions such as, secondary bonds and that one associated to the non-equilibrium state. In particular, in the case of polymer systems, those contributions may be even as important as the strength of primary bonds. Therefore, small structural changes as, for example, the copolymer composition and the length of polymer chains, might have a considerable effect on the CTEs [1, 2].

On the other hand, one interesting feature of polymeric materials is that their CTE is variable when shaped into asymmetric forms; for instance, when they are processed by

Department of Materials Science and engineering and Chemical engineering, IQMAAB, Universidad Carlos III de Madrid, Av. Universidad 30, 28911 Leganés, Spain. E-mail: javid@ing.uc3m.es; Tel: +34 91 624 8870

injection molding and when thin films are made. According to previous reports, this thermal behaviour arises from the preferential in-plane polymer chain orientation or stretching of the macromolecules. In the case of films, for example, the stress anisotropy originated from the oriented polymer chains leads the CTE to depend on the conditions of film deposition and the film thickness [2]. Other studies have shown that CTE and its changes are significantly influenced by the polymer topology as it was observed in poly(*n*-alkyl methacrylate)s by the change of the alkyl chain length [3]. According to the cooperatively rearranging region, CRR, defined by Adam and Gibbs [4], this behaviour was attributed to variations of the cooperative segmental dynamics, ξ_i (CRR) that was observed to decrease as the alkyl chain length is increased [3]. Thus, it was proposed that with a variation of the chemical structure of polymer segments, since the ξ_i (CRR) is modified, the CTE and its changes should be tunable [3]. All these circumstances point out, among others, the necessity of studying the influence of structural changes and molecular size in polymers on their CTE.

One systematic way of introducing structural variations in a polymer is to use a set of random copolymers which composition, in terms of the weight fraction of one comonomer, was different. On the other hand, one parameter referred to the molecular size is the molecular weight. Therefore, the influences on the CTE of two simple variables such as the copolymer composition and the molecular weight are suggested to be studied.

In principle, this topic should not bring any problem since there are several techniques able to deal with the CTE determination. However, when small pieces of material are considered, the change of their dimensions as a function of temperature is usually so poor that the conventional techniques, such as dilatometry and dynamic mechanical analysis, DMA, are not sensible enough as to monitor the corresponding thermal expansion. Due to this, several methods and techniques have been proposed for this purpose, among others: i) image analysis using a CCD camera as described Wang [5] or the digital image correlation method proposed by Pan [6-8]; ii) interferometric techniques [9, 10]; iii) X-ray reflectivity [11, 12]; iv) neutron reflectivity [13]; ellipsometry [14] and vi) the differential capacitance technique [15]. However, none of them have the characteristics of being, easy-handling, accurate, sensitive at the nanoscale and cheap.

Recently, a simple method based on the use of an AFM has been demonstrated to be useful to measure at nanoscale a polymer expansion as a function of temperature [16, 17]. In particular, this method has been successfully used for measuring nano-thermal expansion of nanocomposite films to finally obtain their CTEs. However, the usefulness of this method has not been demonstrated yet on studying nanothermal expansions as a function of structural changes in pure polymers without fillers.

In this work poly(ethylene-co-vinylacetate), EVA, and poly(methyl methacrylate), PMMA, have been chosen because of their multiple uses and academic interest attending to their relatively simple structures. In particular, it is important to

highlight that for certain applications such as hot melt adhesives, encapsulates in solar cells and wires and cables, EVA copolymers are good candidates for their CTE to be tuned. When for these polymers there is the necessity of being applied in the form of thin films with poor thermal expansion, the use of nanoparticles with low CTE as fillers seems to be a very good option. However, sometimes only small changes in the CTE are required. Therefore, the simple variation of the composition of the vinylacetate, VA, comonomer in the EVA copolymer might be enough.

On the other hand, PMMA is a common polymer used for multiple applications in which it is directly join to other materials (ceramics and metals for example) with highly different CTE. Therefore, in both cases, there is the necessity of enlarging our knowledge about the influence structural characteristics of the polymer on their corresponding thermal expansions, probably being the starting point to understand the thermal behaviour of other polymers.

Although this topic is really wide, the aim of the present work is to understand the influence of certain structural changes on the CTE of EVA and PMMA pure polymers without fillers and demonstrate the usefulness of the nanothermal expansion AFM based method to obtain the CTE. This work is focused on revealing some influential factors of CTE but trying to explain them under a physico-chemical perspective, giving equations which were able to estimate CTEs as a function of the structure of polymers. In particular, i) the influence of the structure of EVA copolymer in terms of its composition and ii) the size of PMMA in terms of its molecular weight have been considered. In order to carry out this, by the use of an atomic force microscope, AFM, the linear thermal expansions of films at nanoscale were monitored.

2. Experimental part

2.1. Materials

Poly(ethylene-co-vinyl acetate), EVA with 12, 18, 25 and 40% by weight of vinyl acetate (densities: 0.933, 0.940, 0.948, 0.950 g/cm³ at 25°C respectively) were supplied by Sigma Aldrich. On the other hand, four poly(methyl methacrylates), PMMA, with different molecular weights were used (purchased from Polysciences Inc.). The molecular weights were determined from size exclusion chromatography (Mw: 33.9, 64.8, 75.6 and 360.0 kg/mol and Mn: 17.3, 31.8, 34.5 and 112.600 kg/mol) [18]. Finally, Frekote® 44-NC (Henkel AG & Co. KGaA, Dußseldorf, Germany) was used as demolding agent during the preparation of the polymer films.

2.2. Sample preparation

About 10 mg of the as received polymers were located on an AFM steal disc; after that, a microscope cover slip (treated with demoulding Frekote®) was placed on top. Then, everything was introduced in an oven at 130°C applying pressure with clampers. After 30 minutes of treatment the oven was turned off leaving the sample inside to cool down them slowly until room temperature was reached. Finally, the

microspore slides were removed to have the polymer films with very smooth surfaces well adhered on the AFM discs.

2.3. Measurements

In order to carry out the thermal expansion measurements, an atomic force microscope, AFM, MultiMode Nanoscope IV from Digital Instruments/Veeco Metrology Group was used. Measurements were performed at ambient conditions, in tapping mode, with etched silicon probes (stiffness 40 N/m). The frequency of the probe was adjusted to the resonant frequency in the close vicinity of the samples.

The AFM piezoelectric scanner responds to topography changes of the sample by means of a vertical expansion or contraction to maintain the amplitude set in the initial feedback conditions. Changes in the dimensions of the samples (always associated to the same four scanned lines on the sample) were monitored when heating the sample with a scanner JVH with an inserted heater. A heater controller which allows controlling the temperature of the AFM sample mounting disk with an accuracy of $\pm 0.5^\circ\text{C}$ was used. The manufacturer of the equipment advises to work with the Z-center position as nearer to the value of 0 V as possible. Due to this fact, in order to cover the total range of temperatures, three series of measurements were necessary because the Z-center position is reinitialized each time the AFM tip is engaged. Taking data every degree Celsius three subintervals of temperatures were scanned for every sample. The determination of the linear coefficient of thermal expansion was done using temperatures below 65°C in all cases (above the T_g of EVA and below the T_g of PMMA). Details of the procedure used to determine the coefficient of thermal expansion of thin films can be found in reference [17].

3. Results and discussion

The linear coefficient of thermal expansion, α_L , can be expressed by:

$$\alpha_L = \frac{1}{L_0} \cdot \frac{\Delta L}{\Delta T} \quad (2)$$

This parameter cannot be directly measured because the thickness of the film at room temperature, L_0 , and the linear expansion of the materials with respect to temperature, $\Delta L/\Delta T$, must be obtained independently. Taking into account the equation (1), α_L or the CTE can be obtained from the slope of the curve obtained when the change in the thickness of the films, ΔL , is represented as a function of temperature, T .

Using the atomic force microscope the value of the thermal expansion of the sample, ΔL , can be indirectly measured. A correction of the expansion due to the sample mounting disk, SMD (AFM slide) and other components of the system must be done. The thermal expansion without sample, $\Delta L_{\text{without sample}}$, can be assumed equal to the sum of the thermal expansion of the SMD, ΔL_{SMD} , and the thermal expansion of other components of the system, $\Delta L_{\text{other components}}$.

$$\Delta L_{\text{without sample}} = \Delta L_{\text{SMD}} + \Delta L_{\text{other components}} \quad (3)$$

Therefore, considering the total expansion, ΔL_{total} , the thermal expansion of a material, ΔL , could be obtained from:

$$\Delta L = \Delta L_{\text{total}} - (\Delta L_{\text{without sample}}) \quad (4)$$

Finally, in order to determine the CTE, the combination of equations (3) and (4) is necessary:

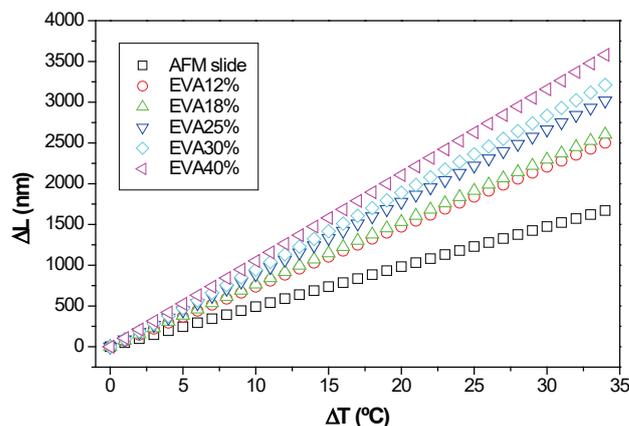


Fig. 1 Thermal expansion for the films of EVA with different compositions of vinylacetate (12, 18, 25, 30 and 40% by weight respectively).

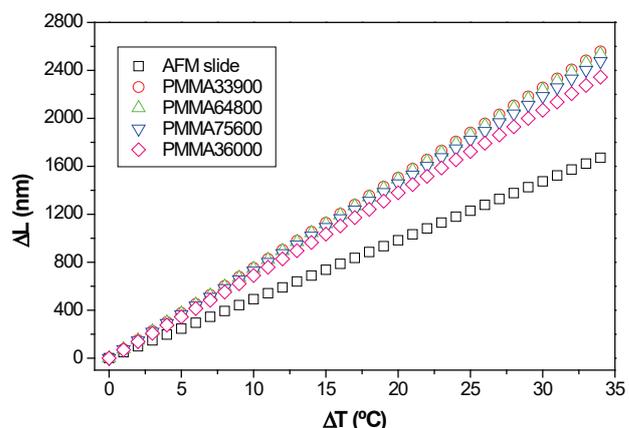


Fig. 2 Thermal expansion for the films of PMMA with different average weight molecular weights, Mw: 33900, 64800, 75600 and 360000 g/mol respectively.

$$\alpha_L = \frac{1}{L_0} \cdot (A - B) \quad (5)$$

Where $A = \frac{\Delta L_{\text{Total}}}{\Delta T}$ and $B = \frac{\Delta L_{\text{without sample}}}{\Delta T}$ are the slopes of the curves obtained from the data given by the AFM when thermal expansion is plotted as a function of the change of temperature, ΔT , with and without sample respectively (Figures 1 and 2). After making a linear fit of the data in the Figures 1 and 2, taking the slopes and applying equation 5, the

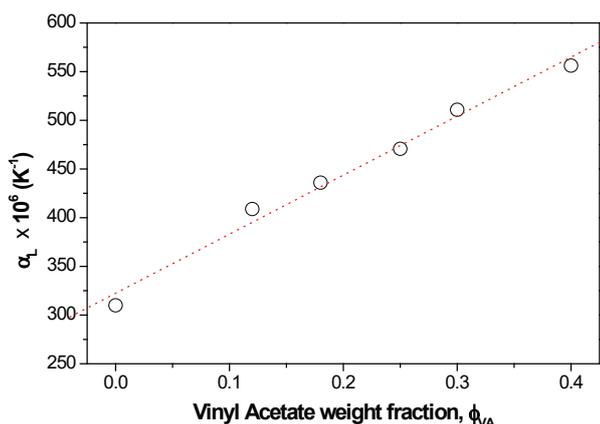


Fig. 3 Coefficient of linear thermal expansion as a function of the vinyl acetate weight fraction (The value of α_L for a 0% of VA or pure PE was taken from reference [17]).

CTEs or α_L of the different samples under study can be obtained.

CTE of EVA as a function of the copolymer composition

In Figure 3 the linear coefficient of thermal expansion, CTE or α_L , is represented as a function of the weight fraction of vinyl acetate, VA. As can be observed, when the percentages of VA are, at least, below 40% there is a linear dependence between the CTE and the weight fraction of VA.

Taking into account that the EVA polymers under study are random copolymers, it is reasonable to consider the systems as homogeneous mixtures of two components. Therefore, a simple rule of mixtures could be used to describe the linear dependence:

$$\begin{aligned} \alpha_L &= \phi_{PE} \cdot \alpha_{PE} + \phi_{VA} \cdot \alpha_{PVAC} \\ \alpha_L &= (1 - \phi_{VA}) \cdot \alpha_{PE} + \phi_{VA} \cdot \alpha_{PVAC} \end{aligned} \quad (6)$$

Where α_L , α_{PE} , α_{PVAC} , are the linear coefficients of thermal expansion of EVA (for a particular weight fraction of VA, ϕ_{VA}), polyethylene, PE, and polyvinylacetate, PVAc, respectively. Rearranging the eq. 4 in terms of ϕ_{VA} , equation 7 is obtained.

$$\alpha_L = \alpha_{PE} + (\alpha_{PVAC} - \alpha_{PE}) \cdot \phi_{VA} \quad (7)$$

Therefore, the experimental values of CTE as a function of VA weight fraction should be able to be fitted to a straight line. In the case of getting a good fitting the zero interception and the slope would give the linear CTEs of polyethylene, α_{PE} , and polyvinylacetate, α_{PVAC} respectively. In Figure 3 it is also shown a dotted line coming from the straight line curve fitting, where the goodness of the fitting can be clearly observed. In fact, the correlation factor was $r=0.993$ what is acceptable for six experimental data. Following the above mentioned procedure, the estimated values for α_{PE} and α_{PVAC} were $(322 \pm 10) \times 10^{-6} \text{K}^{-1}$

and $(929 \pm 100) \times 10^{-6} \text{K}^{-1}$ respectively. The ratio between linear coefficients of thermal expansion of the homopolymers, $\alpha_{PVAC}/\alpha_{PE}$, will be therefore 2.9. In terms of the rule of mixtures it can be assumed that a comonomer unit of vinylacetate expands nearly three times more than an ethylene comonomer unit per degree of temperature increased. In the Figure 4 it is represented a scheme trying to visualize how the rule of mixture operates to give an estimation of the thermal expansion when an EVA copolymer unit is heated from T_1 to T_2 . To have a better idea of the space contribution of each comonomer to the thermal expansion a ratio of 3 between thermal coefficients ($\alpha_{PVAC}/\alpha_{PE}$) was taken because this is nearly the value estimated.

The CTE of PVAc obtained by X-Ray reflectivity in films of about 100 nm of thickness was $730 \times 10^{-6} \text{K}^{-1}$ (heating from 35 to 55°C) [19] while the values of CTE given in bibliography for the PVAc in bulk are $70 \times 10^{-6} \text{K}^{-1}$ at 20 °C and $220 \times 10^{-6} \text{K}^{-1}$ above the glass transition temperature, T_g [20].

It is important to highlight here that the results obtained in this work are closer to those obtained using X-Ray reflectivity in thin films. Apart from possible differences associated to some variation in the structure of the polymers such as the statistical distribution of the comonomer sequences and molecular weights, it seems more reasonable to think that the differences observed in the CTE values arise from the experimental method used to determine them. It is clear that the method under consideration is giving more accurate information at least from the first nanometers of thermal expansion which could be essential when data for coatings and thin films are required.

CTE of PMMA as a function of molecular weight

In Figure 5 the linear coefficient of thermal expansion, α_L is represented as a function of the inverse of the average weight, M_w (left), and number, M_n (right), molecular weights of PMMA. It can be observed that the data of CTE seem to have a linear dependence with the inverse of the molecular weight, $1/M$.

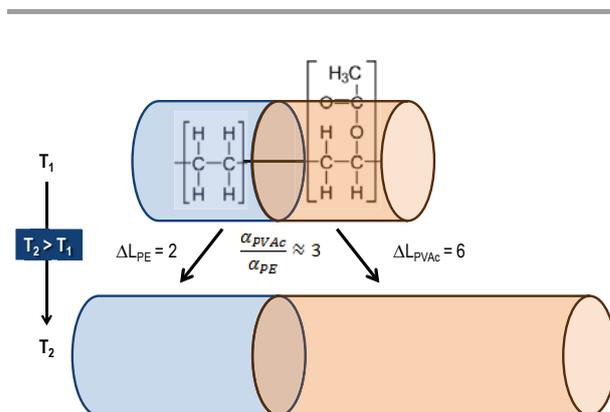


Fig. 4 Scheme trying to visualize how the rule of mixture operates to give an estimation of the thermal expansion when an EVA copolymer unit is heated from T_1 to T_2 .

The results obtained could be easily explained by considering a new model based on the rule of mixtures but making use of the free volume concept as novelty. In this model the main assumption is to consider that the coefficient of thermal expansion in general, or the linear coefficient of thermal expansion in particular, α_L , can be expressed as the sum of the weighted contributions associated to the free and occupied volumes, α_f and α_o respectively.

$$\alpha_L = \phi_f \cdot \alpha_f + \phi_o \cdot \alpha_o \quad (8)$$

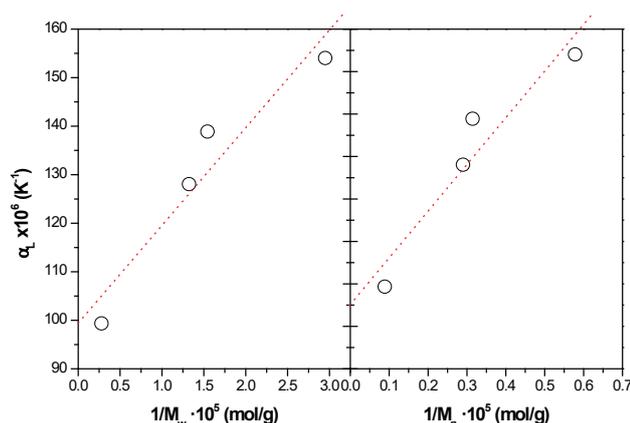


Fig. 5 Coefficient of linear thermal expansion of PMMA as a function of the inverse of the weight, M_w (left), and number, M_n (right), average molecular weights respectively.

Where ϕ_f and ϕ_o are the free and occupied volume fractions, being therefore $\phi_o = 1 - \phi_f$.

On the other hand, below the glass transition temperature or the range of temperatures considered here for the PMMA, it is reasonable to consider that α_f and α_o are constants and they only depend on the nature of the polymer. However, the free volume fraction must depend on the molecular weight if the chain ends are accepted to give extra free volume because of they have more degrees of freedom [21]. Hence, lower molecular weights should imply more chain ends per gram of sample and therefore, higher free volume fraction. Expressing the free volume fraction as a sum of two contributions in which one of them can be named the inherent free volume fraction of the polymer, ϕ_f^0 , and the other one the extra free volume fraction given by the chain ends, ϕ_f^{ext} , equation 8 could be written as follows:

$$\alpha_L = (\phi_f^0 + \phi_f^{\text{ext}}) \cdot \alpha_f + (1 - \phi_f^0 - \phi_f^{\text{ext}}) \cdot \alpha_o \quad (9)$$

In Figure 6 a scheme is presented trying to visualize the concepts of occupied and the different kinds of free volumes.

On the other hand, making use of the free volume concept, it is well known that the excess of volume given by the chain ends per cm^3 of sample can be expressed by:

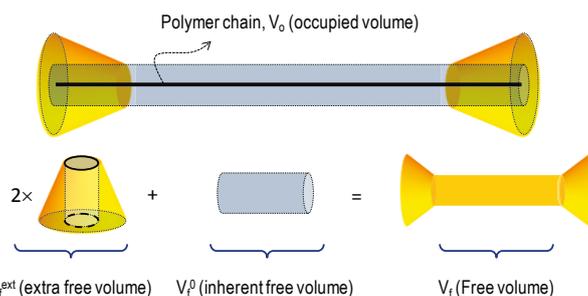


Fig. 6 Scheme trying to visualize the concepts of occupied and the different kinds of free volumes.

$$\phi_f^{\text{ext}} = \frac{K}{M} \quad (10)$$

Where M is the molecular weight and K is a constant related with θ , the free volume excess per chain end, the Avogadro's number, N_{Av} , and the density, ρ , in the following way:

$$K = 2 \cdot \theta \cdot N_{Av} \cdot \rho \quad (11)$$

Therefore, introducing equation 10 in equation 9, the equation 12 is obtained:

$$\alpha_L = A + (\alpha_f - \alpha_o) \cdot K \cdot \frac{1}{M} \quad (12)$$

Where A is a constant since it is a sum of constants:

$$A = \alpha_o + (\alpha_f - \alpha_o) \cdot \phi_f^0 \quad (13)$$

Since $\alpha_f > \alpha_o$, equation 12 has the form of a straight line equation with positive slope. Therefore, representing the coefficient of thermal expansion as a function of the inverse of the molecular weight the data should be well fitted to a straight line as it is reflected in Figure 5 for which the fitting (in both cases with a Pearson's correlation factor of 0.96) is shown as a dotted red line. The goodness of the fitting suggests that the expansion of a polymer, at least at nanoscale, can be well and easily described by the sum of the weighted contributions of the occupied and free volumes.

4. Conclusions

From linear thermal expansion measurements at nanoscale, the influences of the structure of poly(ethylene-co-vinylacetate), EVA, in terms of its composition (vinylacetate content) and the size of poly(methyl methacrylate), PMMA, in terms of its molecular weight, on their linear coefficient of thermal expansion, CTE, were investigated. It has been

demonstrated that an AFM can be used to monitor nanothermal expansions to study CTE as a function of structural changes in pure polymers without fillers. The dependence of the CTE of EVA on the weight fraction of vinyl acetate was explained with a simple model based on the rule of mixtures where the components of the mixture are the comonomers of the copolymer. A simple equation considering the weighted contributions of each EVA comonomer was enough to estimate the final CTE. On the other hand, the dependence of the CTE of PMMA on the molecular weight was explained with a new, intuitive and very simple model based on the rule of mixtures and the free volume concept. In this case, the components of the mixture were the free and occupied volumes respectively.

Acknowledgements

Authors gratefully acknowledge financial support of the Ministerio de Ciencia e Innovación (MAT2010-16815) y Ministerio de Economía y Competitividad (MAT2014-59116-C2-1-R).

Notes and references

- 1 J. Ishii, A. Takata, Y. Oami, R. Yokota, L. Vladimirov, M. Hasegawa, *Eur. Polym. J.*, 2010, **46**, 681.
- 2 Y. Jung, Y. Yang, S. Kim, H. Kim, T. Park, B.W. Yoo, *Eur. Polym. J.*, 2013, **49**, 3642.
- 3 C.G. Campbell, B.D. Vogt, *Polymer*, 2007, **48**, 7169.
- 4 G. Adam, J.H. Gibbs, *J. Chem. Phys.*, 1965, **43**, 139.
- 5 H. Wang, G.H. He, B.L. Zhou, X. Chen, W.M. Liu., *Rev. Sci. Instrum.*, 1993, **64**, 3617.
- 6 P. Bing, X. Hui-min, H. Tao, A. Asundi, *Polym. Test.*, 2009, **28**, 75.
- 7 M. Jarabek, Z. Major, R.W. Lang, *Polym. Test.*, 2010, **29**, 407.
- 8 S.R. Henz, J.S. Wiggins, *Polym. Test.*, 2010, **29**, 925.
- 9 S.T. Chen, H.H. Wagner, *J. Electron. Mater.*, 1993, **22**, 797.
- 10 C.C. Lee, C.L. Tien, W.S. Sheu, C.C. Jaing, *Rev. Sci. Instrum.*, 2001, **72**, 2128.
- 11 W.E. Wallace, J.H. van Zanten, W.L. Wu, *Phys. Rev. E*, 1995, **52**, R3329.
- 12 M. Mukherjee, M. Bhattacharya, M.K. Sanyal, *Phys. Rev. E*, 2002, **66**, 061801.
- 13 L. Singh, P.J. Ludovice, C.L. Henderson, *Thin Solid Films*, 2004, **449**, 231.
- 14 T. Kanayaa, T. Miyazakia, H. Watanabe, K. Nishida, H. Yamanoa, S. Tasakic, D.B. Bucknall, *Polymer*, 2003, **44**, 3769.
- 15 H. Lioua, P.S. Hoa, R. Stierman, *Thin Solid Films*, 1999, **339**, 68.
- 16 J. González-Benito J, E. Castillo, J.F. Caldito, *Eur. Polym. J.*, 2013, **49**, 1747.
- 17 D. Olmos, F. Martínez, G. González-Gaitano, J. González-Benito, *Eur. Polym. J.*, 2011, **47**, 1495.
- 18 D. Olmos, K. Bagdi, J. Mózcó, B. Pukánszky, J. González-Benito, *J. Colloid Inter. Sci.*, 2011, **360**, 289.
- 19 M. Mizusawa, K. Sakurai, *Mater. Sci. Eng.*, 2010, **24**, 012013.
- 20 J. Brandrup, E.H. Immergut, E.A. Grulke, A. Abe, D.R. Bloch. *Polymer Handbook*, John Wiley & Sons Inc. 1999, 1, V/77.
- 21 T.G. Fox, P.J. Flory, *J. Polym. Sci.*, 1954, **14**, 315.